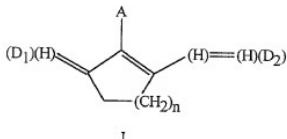


CLAIMS

What is claimed is:

1. A near infrared sensitive composition, comprising:

- 5 (a) a near infrared dye photochemical sensitizer which is substantially free of borate anion that enables the composition to undergo either
 - (i) effective photopolymerization or
 - (ii) effective photoimaging upon exposure to near infrared radiation, the near infrared dye is a compound of formula I:



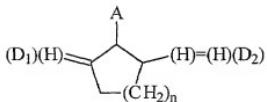
wherein substituent A is chosen from

- (1) a 5-6 membered heterocyclic ring system having 1-3 ring heteroatoms, in which the heteroatom is a nitrogen atom, which is substituted with a hydrogen atom, C₁-C₆ alkyl, (CH₂)_mCO₂H or (CH₂)_mCO₂(C₁-C₆ alkyl) and the carbon atom of the heterocyclic ring system may be substituted with an oxygen atom to form a carbonyl or enolate anion and m is an integer ranging from 0-4;
- (2) a 5-6 membered carbocyclic moiety substituted with a hydrogen atom or a C₁-C₆ alkyl group wherein a carbon atom of the alkyl group may be substituted with oxygen to form a carbonyl or enolate anion;
- (3) a quinoline or isoquinoline group wherein the nitrogen atom is directly bonded to the carbocyclic moiety of formula I;
- (4) N,N-bisaryl or bis(C₁-C₆ alkyl) or bisaryl(C₁-C₆ alkyl) amine wherein the aryl

DRAFT 2020

- group is a naphthyl or phenyl group which is unsubstituted or substituted with a fluorine atom, bromine atom, chlorine atom, OCH₃, CF₃, OH, or C₁-C₆ alkyl;
- 5 (5) a heterocyclic ring system having at least one nitrogen atom bonded directly to the carbocyclic ring of formula I and a group Z which is a carbon atom, NR⁸, oxygen atom or sulfur atom wherein R⁸ is a hydrogen atom, C₁-C₆ alkyl, CO₂H or CO₂C₁-C₆ alkyl;
- 10 substituent D₁ is a 9-15 membered heterocyclic system comprising a heteroaryl ring system having at least one heteroatom group (U) which is an NR³ group, oxygen atom, sulfur atom or PR³ group which is directly bonded to the aryl portion of the heteroaryl ring system and wherein R³ is a C₁-C₆ alkyl which may be unsubstituted or substituted with CO₂H, SO₃H or salts thereof and wherein the aryl ring may be unsubstituted or substituted with OCH₃, CF₃, bromine atom, chlorine atom, fluorine atom, C₁-C₆ alkyl or OH or a fused ring polycyclic heterocyclic system;
- 15 20 substituent D₂ has the identical heterocyclic system as substituent D₁ except that when U is NR³, the nitrogen atom is quaternized to form an amine salt which is neutralized by an enolate anion from A when A is a substituted pyrimidine like moiety or by a discrete (non intra-molecular) anion;
- 25 n is an integer ranging from 1-2;
- (b) a hexaarylbimidazole compound as photoinitiator;
- 30 (c) a photopolymerizable material and a chain transfer agent, or, instead of (c),
- (d) a photoimageable dye.
2. A photopolymerizable element comprising:
- (a) a support,
- 35 (b) a photopolymerizable composition comprising
- (i) a near infrared dye photochemical sensitizer which is substantially free of borate anion that enables the photopolymerizable composition to

undergo effective photopolymerization upon exposure to near infrared radiation, the near infrared dye is a compound of formula I:



I

5

wherein A is:

- (1) a 5-6 membered heterocyclic ring system having 1-3 ring heteroatoms, in which the heteroatom is a nitrogen atom which is substituted with a hydrogen atom, C_1-C_6 alkyl, $(CH_2)_mCO_2H$ or $(CH_2)_mCO_2(C_1-C_6$ alkyl) and the carbon atom of the heterocyclic ring system may be substituted with an oxygen atom to form a carbonyl or enolate anion and m is 0-4;
- (2) a 5-6 membered carbocyclic moiety substituted with hydrogen atom, C_1-C_6 alkyl group wherein the carbon atom of the alkyl group may be substituted with oxygen to form a carbonyl or enolate anion;
- (3) quinoline or isoquinoline groups wherein the nitrogen atom is directly bonded to the carbocyclic moiety of formula I;
- (4) N,N-bisaryl or bis(C_1-C_6 alkyl) or bisaryl(C_1-C_6 alkyl) amine wherein the aryl group is a napthyl or phenyl group which is unsubstituted or substituted with fluorine atom, bromine atom, chlorine atom, OCH_3 , CF_3 , OH , C_1-C_6 alkyl;
- (5) a heterocyclic ring system having at least one nitrogen atom bonded directly to the carbocyclic ring of formula I and a group Z which is a carbon atom, NR^8 , oxygen atom, or sulfur atom wherein R^8 is a hydrogen atom, C_1-C_6 alkyl, CO_2H or $CO_2C_1-C_6$ alkyl;
- 25 substituent D_1 is a 9-15 membered heterocyclic system comprising a heteraryl ring having at least one heteroatom group (U) which is an NR^3 group, oxygen atom, sulfur atom, or PR^3 group which is directly bonded to the aryl portion of the heteraryl ring system and wherein R^3 is a C_1-C_6 alkyl which may be unsubstituted or substituted with CO_2H , SO_3H or salts thereof and wherein the
- 30

aryl ring may be unsubstituted or substituted with OCH₃, CF₃, bromine atom, chlorine atom, fluorine atom, C₁-C₆ alkyl or OH or a fused ring polycyclic heterocyclic system;

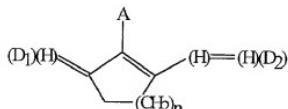
- 5 substituent D₂ has the identical heterocyclic system as substituent D₁
except that when U is NR₃, the nitrogen atom is quaternized to form an amine salt which is neutralized by an enolate anion from A when A is a substituted pyrimidine like moiety or by a discrete (non intra-molecular) anion;

n is an integer ranging from 1-2;

- 10 (c) a hexaarylbiimidazole compound as photoinitiator;
(d) a photopolymerizable material and a chain transfer agent;
and
(e) a binder polymer.

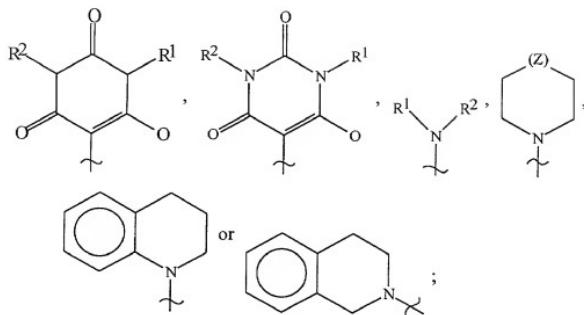
3. A near infrared sensitive composition, comprising:

- 15 (a) a near infrared dye photochemical sensitizer which is substantially free of borate anion that enables the composition to undergo either
(i) effective photopolymerization or
(ii) effective photoimaging upon exposure to near
infrared radiation, the near infrared dye is a compound
of formula I:

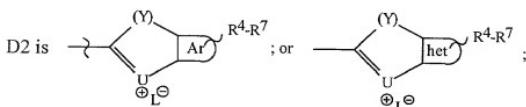
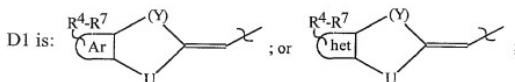


I

wherein substituent A is



5

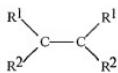


R¹ or R² are independently selected from H, C₁-C₆ alkyl; or
aryl wherein aryl is phenyl or naphthyl which may be unsubstituted or
10 substituted with halogen, -O(C₁-C₆ alkyl), -Oaryl, aryl or CF₃;
(C₁-C₆ alkyl) (C₁-C₁₀ aryl) or hydrogen;

is an aromatic ring chosen from phenyl or naphthyl;

is a heteroaryl ring chosen from benzopyrazine, benzo-1,4-oxazine
or benzo-1,4-thiazine.

15 U is selected from NR³, S, PR³ or O;
Y is selected from C(R¹)(R²);



or U, wherein R¹ and R² are as defined above;

5 R³ is selected from C₁-C₆ alkyl unsubstituted or substituted with CO₂H, SO₃H or salts thereof;

R⁴-R⁷ are independently chosen from H, OCH₃, CF₃, halogen; Z is chosen from NR⁸, C, O or S;

R⁸ is chosen from H, C₁-C₆ alkyl, (CH₂)_mCO₂H or (CH₂)_mCO₂(C₁-C₆ alkyl); and

m is 0-6;

10 n is 1-2;

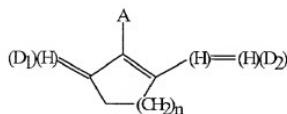
provided that when A contains an enolate anion, a counterion L[⊖] is not present;

- (b) a hexaarylbiimidazole compound as photoinitiator;
- (c) a photopolymerizable material and a chain transfer agent; or, instead of (c),
- (d) a photoimageable dye.

4. A photopolymerizable element comprising:

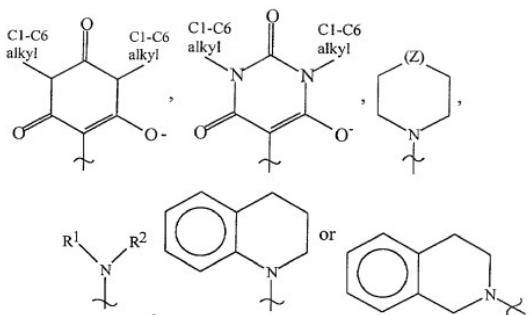
- (a) a support;
- (b) a photopolymerizable composition comprising

20 (i) a near infrared dye photochemical sensitizer which is substantially free of borate anion that enables the photopolymerizable composition to undergo effective photopolymerization upon exposure to neared infrared radiation, the near infrared dye is a compound of formula I:



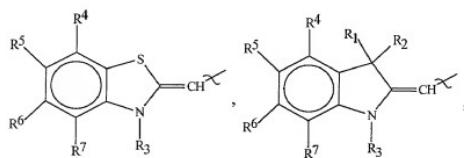
I

wherein A is

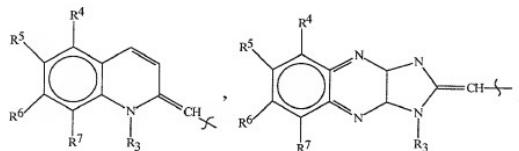


5

D₁ represents a heterocyclic ring structure selected from the group consisting of:

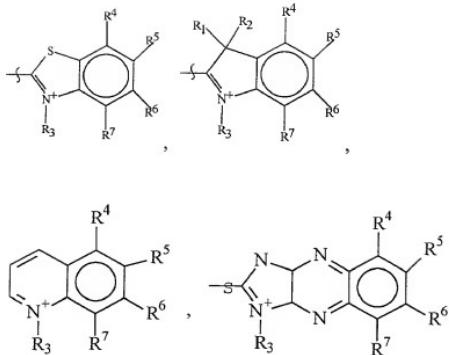


10



D₂ represents a heterocyclic ring structure selected from the group consisting of

15

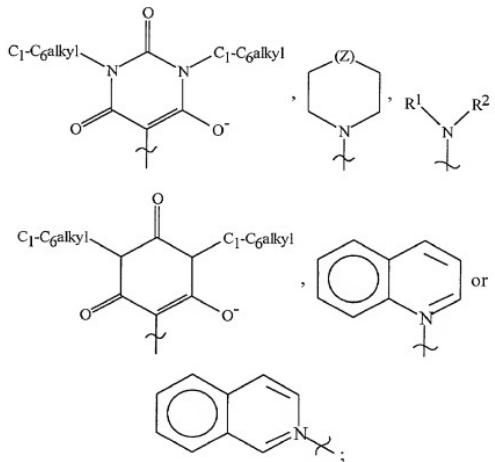


- 5 R¹ or R² are independently selected from:
 C₁-C₆ alkyl, aryl wherein aryl is phenyl or naphthyl which may be
 unsubstituted or substituted with halogen, -O(C₁-C₆ alkyl), Oaryl, aryl or CF₃,
 (C₁-C₆ alkyl) aryl or hydrogen;
- 10 R₃ is C₁-C₆ alkyl, C₁-C₆ alkylsulfonate, C₁-C₆ alkyloxycarbonyl, C₁-C₆
 alkyl, or C₁-C₆ alkylcarboxy;
- 15 Z is selected from NR⁸, C, O or S wherein R⁸ is H, C₁-C₆ alkyl, CO₂H or
 CO₂(C₁-C₆ alkyl);
 R⁴-R⁷ are independently selected from H, OCH₃, CF₃; or any two of
 R⁴-R⁷ which when ortho substituents may join to form a phenyl ring; n is an
 integer ranging from 1-2
 with the proviso that D₂ is selected to be the quaternized heterocyclic ring structure
 that corresponds to D₁ such that D₁ and D₂ together form a pair of heterocyclic
 ring structures;
- 20 (c) a hexaarylbimidazole compound as photoinitiator;
 (d) a photopolymerizable material and a chain transfer agent; and
 (e) a binder polymer.
- 25 5. A near infrared sensitive composition, comprising:
 (a) a near infrared dye photochemical sensitizer which is substantially
 free of borate anion that enables the composition to undergo either
 (i) effective photopolymerization or
 (ii) effective photoimaging upon exposure

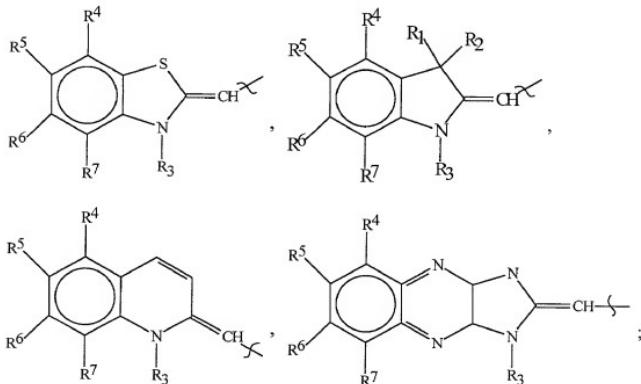
to near infrared radiation wherein the near infrared dye is selected from the group consisting of DF-1413, DF-1419, DF-1422, DF-1429, DF-1668, DF-12124, DF-15118, DF-15131, DF-15132, NK-3877, GW-826, GW-436, GW-776, GW-976, GW-186, and NK-2268;

- 5 (b) a hexaarylbimidazole compound selected from the group consisting of o-Cl-HABI, CDM-HABI, 2,3,5-TCI-HABI, and TCTM-HABI; and
 (c) a photopolymerizable material selected from the group consisting of tripropylene glycol diacrylate, trimethylolpropane triacrylate, ethoxylated trimethylolpropane triacrylate, propoxylated trimethylolpropane triacrylate,
10 ethoxylated Bisphenol A dimethacrylate, and triethylene glycol dimethacrylate, and a chain transfer agent selected from the group consisting of N-phenylglycine, julolidine, 2-mercaptopbenzoxazole, 2,6-diisopropyl-N,N-dimethylaniline, a borate salt and an organic thiol.

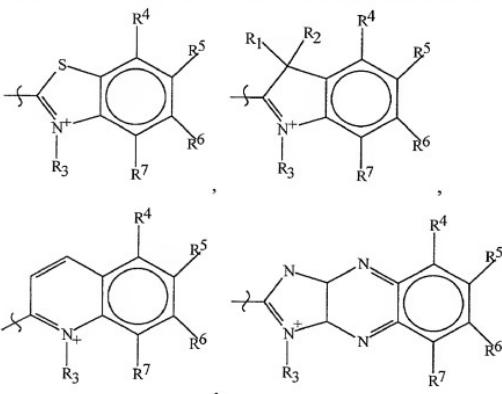
6. The composition according to Claim 3 wherein A is selected from the
15 group consisting of



D₁ represents a heterocyclic ring structure selected from the group consisting of



D₂ represents a heterocyclic ring structure selected from the group consisting of



R₁ or R₂ are independently selected from:

C₁-C₆ alkyl;

10 aryl wherein aryl is phenyl or naphthyl which may be unsubstituted or substituted with halogen, -O(C₁-C₆ alkyl), Oaryl, aryl or phenyl, CF₃ (C₁-C₆ alkyl)(C₁-C₁₀ aryl) or hydrogen;

R₃ is C₁-C₆ alkyl, C₁-C₆ alkylsulfonate, C₁-C₆ alkyloxycarbonyl, C₁-C₆ alkyl, or carboxy C₁-C₆ alkyl;

Z is selected from NR⁸, C, O or S wherein R⁸ is H, C₁-C₆ alkyl, CO₂H or CO₂(C₁-C₆ alkyl);

R⁴-R⁷ are independently selected from H, OCH₃, CF₃; or any two of R⁴-R⁷ which when ortho substituents may join to form a phenyl ring;

- 5 with the proviso that D₂ is selected to be the quaternized heterocyclic ring structure that corresponds to D₁ such that D₁ and D₂ together form a pair of heterocyclic ring structures.

7. The composition according to Claim 3, wherein the near infrared dye is selected from the group consisting of DF-1413, DF-1419, DF-1422, DF-1429,

- 10 DF-1668, DF-12124, DF-15118, DF-15131, DF-15132, NK-3877, GW-826, GW-436, GW-776, GW-976, GW-186, and NK-2268; the hexaarylbimidazole compound is selected from the group consisting of o-Cl-HABI, CDM-HABI, 2,3,5-TCl-HABI, and TCTM-HABI; wherein the photopolymerizable material is selected from the group consisting of tripropylene glycol diacrylate,

- 15 trimethylolpropane triacrylate, ethoxylated trimethylolpropane triacrylate, propoxylated trimethylolpropane triacrylate, ethoxylated Bisphenol A dimethacrylate, and triethylene glycol dimethacrylate, and the chain transfer agent is selected from the group consisting of N-phenylglycine, julolidine, 2-mercaptopbenzoxazole, 2,6-diisopropyl-N,N-dimethylaniline, and an organic thiol; or the photoimageable dye is selected from the group consisting of LCV, LECV, LPCV, LBCV, LV-1, LV-2 and LV-3.

8. The composition according to Claims 1, 2, 3 or 4 wherein the near infrared dye is present in at least 0.5% by weight of the total composition; the hexaarylbimidazole compound is present in at least 0.5% by weight of the total composition; and the photopolymerizable material is present in at least 20% by weight of the total composition and the chain transfer agent is present in at least 0.1% by weight of the total composition; or the photoimageable dye is present in at least 0.5% by weight of the total composition.

9. The composition according to Claims 1, 2, 3, 4 or 5 which further comprises a binder polymer.

10. The composition according to Claims 1, 2, 3 or 4 wherein the composition, containing at least 0.5 weight percent of the near infrared dye, undergoes either (1) effective photopolymerization or (2) effective photoimaging to a photopolymerized or photoimaged photopolymer upon exposure to near infrared actinic radiation at a fluence of at least 100 mW/cm² (fluence units) for a period of at least 2 seconds (time units).